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Final Report

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Acres International Limited
480 University Avenue
Toronto, Ontario M5G 1V2

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EVALUATION OF ZEOLITE AND SODIUM HYDROXIDE CHEMICAL HEAT PUMPS (UP-06-021)

FINAL REPORT BY

ACRES INTERNATIONAL LIMITED

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SCIENTIFIC-ADVISOR:	K. Snelson National Research Council Low Temperature Laboratory

PROJECT TEAM

The team assembled for this project by Acres International Limited was composed of

Project Manager	D.C.K. Ngo
Project Engineer	A. T. Carter
Project Technical Co-ordinator	J. B. Codrington
Economist	S. G. Ferguson
Consultant	R. L. Gudgeon
Special Consultants	Dr. J. M. Shaw University of Toronto
	Dr. E. G. Plett ASECOR Ltd.

EXECUTIVE SUMMARY

The study focusses on a comparison of two potentially viable chemical heat pump systems, one using liquid Sodium Hydroxide (NaOH) and the other using solid (granular) Zeolite as the heat upgrading medium.

An earlier study on the Sodium Hydroxide Chemical heat pump was carried out by Acres International Limited for the National Research Council. This report was published in 1985 and was called the Phase 'A' study.

As part of the present study, an independent review of the Phase 'A' study work was carried out at the Chemical Engineering Department of the University of Toronto. This review concentrated on the absorber design methods developed during this Phase of the work because this component was the only one in the system for which proven design methods do not exist. The review confirmed the viability of the design approach.

The University of Toronto review also proposed a laboratory scale contacting tower. This would be built and operated at the University of Toronto to refine the design methods, carry out investigations into materials compatibility, and evaluate various performance aspects of the tower. The estimated costs for building and operating the model are $40,000 and $10,000 respectively.

Investigations into the properties of zeolite identified a wide range of natural and synthetic zeolites with a broad range of properties. Synthetic zeolites in the form of molecular sieve are the types most commonly identified for heat transfer work in technical publications.

The applications of zeolite to the heat pumping process was evaluated, and a performance evaluation of a heat pump drier unit was carried out through the use of a computer program developed earlier during zeolite work for the Natural Research Council, which was modified for heat pump applications.

A rotating heat wheel concept was the device selected for computerized evaluation, because it avoids the multiplicity of units which would be required to provide a continuous flow from the basically discontinuous zeolite bed,

A review of published technical papers on zeolite chemical heat pumps was carried out, and whilst the application of zeolite to heat storage systems was found to be quite common, only a few papers described heat pump applications.

The theoretical performance of Zeolite and Sodium Hydroxide chemical heat pumps was compared, using the bench scale drier system from the earlier study as the basis. For this application the dimensions of the zeolite heat wheel and the Sodium Hydroxide absorption tower are comparable in size.

Recommendations for future activities include construction and testing of a laboratory scale Sodium Hydroxide contacting tower, refining of the computer code and construction of a small thermal wheel for the zeolite heat pump, and investigations into cheaper Sodium Hydroxide compatible construction materials.

It is concluded that both the Sodium Hydroxide and zeolite heat pump concepts are technically feasible but more data are required to carry out a detailed comparison. Neither concept should be rejected at this point in time.

RESUME

La présente étude se concentre sur une comparaison de deux systèmes de pompes à chaleur qui pourraient être réalisables, l'un utilisant de l'-hydroxide de sodium (NaOH), et l'autre utilisant de la zéolite solide (en grains) comme le moyen pour rehausser la chaleur.

La Compagnie Acres International Limitée a réalisé une étude antérieure pour le Conseil national de recherches Canada au sujet d'une pompe à chaleur à hydroxide de sodium. Le rapport sur cette étude fut publié en 1985 sous le nom de "Etude Phase A".

Comme partie de la présente étude, le Département de génie chimique de l'Université de Toronto a fait un examen indépendant des études réalisées pour l'étude Phase A. Cet examen se concentrait sur les méthodes de conception de l'absorbeur qui était développé au cours de cette phase du travail, parce que cela représentait la seule partie composante du système pour laquelle il n'existent pas de méthodes de conception qui sont mises à l'épreuve. L'examen a confirmé que la méthode de conception utilisée est praticable.

De plus, les conclusions émanant de l'examen de l'étude par l'Université de Toronto proposèrent la construction d'un tour de contact à l'échelle de laboratoire. Cette tour serait construite et exploitée sur les lieux de l'Université de Toronto, ayant pour but la mise au point des méthodes de conception, l'exécution de travaux d'investigation en ce qui concerne la compatibilité des matériaux, et l'évaluation des différents aspects du fonctionnement de la tour. On estime que les coûts de construction et d'exploitation du modèle seront de $40 000 et $10 000 respectivement.

Des investigations en ce qui concerne les propriétés de la zéolite ont identifié toute une gamme de zéolites naturelles et synthétiques avec un grand écart de propriétés. Dans les publications techniques on identifie le plus souvent des zéolites synthétiques en forme d'un tamis moléculaire qui sont utilisées pour le transfert de la chaleur.

On a fait une évaluation des applications de la zéolite en ce qui concerne le processus de pompage de la chaleur et on a fait une évaluation du fonctionnement de l'élément de séchage d'une pompe à chaleur par l'intermédiaire d'un programme informatisé qui avait été développé au cours des études sur la zéolite réalisées antérieurement pour le Conseil national de recherches, programma qui avait été modifié spécifiquement aux fins des applications aux pompes à chaleur.

Pour faire une analyse informatisée on a choisi le concept d'une roue à chaleur tournant, parce que ce dispositif évite la multitude d'unités qui seraient nécessaires pour donner une circulation continue venant du lit de zéolite qui est à la base discontinu.

Un examen des articles techniques publiés au sujet de pompes à chaleur chimiques utilisant de la zéolite a montré que, bien qu'on ait trouvé que l'application de la zéolite aux systèmes de stockage de la chaleur est assez commun, il n'y a que peu d'articles qui donnent une description de l'application de la zéolite aux pompes à chaleur.

Le fonctionnement théorique de pompes à chaleur chimiques utilisant de la zéolite et celles qui utilisent de l'hydroxide de sodium a été comparé, se basant sur le système de séchage à l'échelle de laboratoire de l'étude antérieure . Aux fins de cette application, les dimensions de la roue à chaleur à zéolite et de la tour d'absorption d'hydroxide de sodium sont comparables.

Parmi les recommandations pour des activités au futur il y a la construction et la mise à l'essai d'une tour de contact d'hydroxide de sodium à l'échelle de laboratoire, la mise au point d'un code informatisé et la construction d'une petite roue thermique pour la pompe à chaleur à zéolite, ainsi que des investigations au sujet de matériaux de construction compatibles avec de l'hydroxide de sodium qui sont moins dispendieux.

L'étude aboutit à la conclusion que le concept d'une pompe à chaleur à zéolite ainsi qu'à hydroxide de sodium est réalisable d'une point de vue technique; toutefois on aura besoin de plus de données afin de réaliser une comparaison plus détaillée. Il ne conviendrait pas de rejeter ni l'un ni l'autre des deux concepts à ce point.

TABLE OF CONTENTS

	Page
1 - INTRODUCTION	1
2 - SODIUM HYDROXIDE CHEMICAL HEAT PUMP	2
2.1 - Review of Phase 'A' Study	2
2.2 - Laboratory Scale Contacting Tower	3
2.3 - Estimated Cost of Laboratory-Scale Model Test Program	5
3 - ZEOLITE CHEMICAL HEAT PUMPS	6
3.1 - Zeolite Materials	6
3.2 - The Use of Zeolite in a Chemical Heat Pump	8
3.2.1 - Introduction	8
3.2.2 - Principle of Zeolite Heat Pumping	10
3.2.3 - Practical Application of Zeolite to Heat Pumping Processes	11
3.3 - Review of Published Technical Data	13
3.4 - Performance of a Zeolite Heat Pump and Comparison with the Sodium Hydroxide System	18
3.4.1 - Performance of a Zeolite Heat Pump	18
3.4.2 - First Order Zeolite Wheel Design	19
3.4.3 - Results for the First Order Design	20
3.4.4 - Comparison with the N_aOH System	22
3.4.5 - Relative Advantages/Disadvantages of Zeolite and N_aOH Systems	23
4 - RECOMMENDATIONS & CONCLUSIONS	26
4.1 - Recommendations	26
4.2 - Conclusions	27
BILIOGRAPHY	29
APPENDIX A	31
APPENDIX B	42

LIST OF TABLES

3.1 IMPORTANT NATURAL ZEOLITES

3.2 COMMERCIALLY AVAILABLE MOLECULAR SIEVES

4.1 INDUSTRY: NON-METALLIC MINERALS AND PRODUCTS

4.2 INDUSTRY: CHEMICALS AND CHEMICAL PRODUCTS

4.3 INDUSTRY: METALLIC MINERALS

4.4 INDUSTRY: TEXTILES, RUBBER AND PLASTICS, METAL PRODUCTS

4.5 INDUSTRY: WOOD PRODUCTS, PULP AND PAPER

4.6 INDUSTRY: FOOD PRODUCTS, BEVERAGES AND GRAINS

LIST OF FIGURES

3.1 ALTERNATING ZEOLITE BEDS USED FOR HEAT PUMPING

3.2 ZEOLITE THERMAL WHEEL

3.3 CLOSED CYCLE ZEOLITE HEAT PUMP

3.4 ZEOLITE WHEEL OUTLET AIR TEMPERATURE VARIATION WITH TIME

LIST OF APPENDICES

APPENDIX A - POTENTIAL APPLICATIONS

APPENDIX B - REVIEW OF PHASE 'A' STUDY

1 - INTRODUCTION

1 - INTRODUCTION

In September 1986, Acres International Limited submitted an unsolicited proposal to Department of Supply and Services Canada for a research program on Chemical Heat Pumps.

The research program proposed was a comparison of two potentially viable Chemical Heat Pumps, namely, the sodium hydroxide system and the Zeolite system.

The National Research Council (NRC) had previously carried out work on the sodium hydroxide heat pump, and on zeolite systems, but they had not been developed to an equal state of development as heat pump systems.

The main points of difference were that the sodium hydroxide (N_aOH) system had only been modelled analytically and had not been verified by a laboratory test model, whilst the zeolite system had been analytically modelled and verified in the laboratory, but had not been evaluated as a potential industrial heat pump candidate to the same extent as the N_aOH system.

The intent basis of the proposal, and the work subsequently authorized by Supply and Services Canada, was to investigate means by which the two systems could be brought to an equal state of advancement, and to carry out a comparison of the two types and their industrial potential. Recommendations on future research and development activities were also to be provided.

2 - SODIUM HYDROXIDE CHEMICAL HEAT PUMP

2 - SODIUM HYDROXIDE CHEMICAL HEAT PUMP

2.1 - Review of Phase 'A' Study

In order to obtain an independent evaluation of the design methods developed in the Phase 'A' study, particularly for the most crucial item in the process, the absorber, chemical engineering expertise was solicited. The University of Toronto has a large Chemical Engineering Department of high reputation. The university agreed to carry out a review of the study, in addition to providing details of an appropriate laboratory scale test unit and test program (see 2.2 below).

The review as requested was restricted to the proposed absorber design, as the remainder of the plant design (i.e. regenerator, condenser, etc) can be designed using methods currently in use and fully proven. The reviewer was Professor J. M. Shaw who agreed that the absorber was the only piece of equipment for which proven design methods are not available. Professor Shaw's report entitled 'Sodium Hydroxide Chemical Heat Pump - A Review of the Phase A Study including a Revised Laboratory Scale Test Apparatus' is attached as Appendix 'B' to this report.

The comments made by Professor Shaw in his review, and in subsequent meetings are summarized in the following.

The reason for lack of published information on the absorber process is not due to the process itself being unproven. In the chemical process industries, absorption is a commonly applied operation for which considerable data are available, including the sodium hydroxide/water absorption process. However, the concentrations of around 60% sodium hydroxide, as proposed for the heat pump being reviewed, is outside of those commonly in use, and a literature search did not reveal any references on the subject at such levels of concentration. Professor Shaw indicated that this is not an uncommon occurrence when trying to obtain data at high concentrations for numerous other chemicals. It

does not necessarily reflect an impracticability for the process but rather that it is not in common use.

Professor Shaw checked the mass and energy balances provided in the study, and found them to be approximately correct. The study proposed a concurrent flow arrangement within the absorber for the air and the sodium hydroxide streams. While Professor Shaw confirmed that the chosen dryer application would work in concurrent flow, countercurrent flow would be necessary in some applications and would be the preferred method of operation for a system which would satisfy all potential applications.

The height of a transfer unit and therefore the packing depth required was estimated by Professor Shaw to be substantially lower than that indicated in the phase A study. Without the results from a laboratory scale test unit it is not possible to predict what the packing depth would be, except to say it would be less than that estimated. This would be beneficial to the sodium hydroxide chemical heat pump concept in that it would reduce the size and cost of the absorber, the largest and most expensive component.

With regard to materials of construction, the use of nickel above 120^{o}C is not recommended and, while this temperature is higher than that existing in the proposed application, it would be a limiting factor for other possible applications. The use of materials test samples in the laboratory-scale test unit is recommended, and this topic will be addressed further in Section 4.0 Recommendations and Conclusions.

2.2 - Laboratory Scale Contacting Tower

Professor Shaw proposed a test of a laboratory-scale unit for the absorber tower, together with a test program. The proposed apparatus is a 0.04% scale model of the absorber section of the system selected for use in the Phase A dryer application.

The tower would be constructed from monel (a nickel alloy) tube and would contain a packing consisting of 0.25-in. monel Rashig rings (Rashig rings are commonly used in the chemical industry). A total of 17 sample ports will be located equally spaced along the tube for sampling the conditions at various stages in the process. Although demisting is not considered by Professor Shaw to be a problem of any significance in this application, a standard demisting mesh will be provided at the outlet from the tower to prevent sodium hydroxide carryover.

The model is an open system wherein air and steam are mixed to achieve the required moisture content and then heated to the correct temperature. The air stream is monitored for moisture and temperature changes and on leaving the tower is vented rather than recirculated. Sodium hydroxide is premixed to the required concentration and pumped into the model. Upon leaving the tower in a diluted condition it is mixed with fresh sodium hydroxide pellets to raise the concentration to the original level, and then recirculated through the tower.

Flow controllers are placed on the air, steam and sodium hydroxide feed lines. All stream temperatures, the compositions of the two moist air streams, and temperatures at 4 elevations in the absorber will be logged on a microcomputer.

The largest single cost item is the instrumentation to measure the moisture content of the air stream. Following discussions between Professor Shaw, representatives of Acres International Limited, and the National Research Council, it was agreed that outright purchase of these instruments for the laboratory test model is probably not the most economic solution. The possible loan of the equipment by NRC (if available) was agreed to be a more practical solution. In the phase A study it was Acres recommendation to rent instrumentation, although purchase of the less expensive instruments and data acquisition components is probably more appropriate and easier to manage.

2.3 - Estimated Cost of Laboratory-Scale Model Test Program

As mentioned previously it is probably not appropriate to purchase the moisture measuring devices exclusively for the test program, therefore their cost can be excluded from the estimated cost of the test model. The estimated cost for materials, equipment, assembly and initial testing of the model is estimated to be $17,330.

The test program is estimated to last approximately 2 months, though this would depend upon whether or not additional tests such as materials testing are called for. Based on a 2-month period, and including manpower costs and consumable's, etc, the estimated cost of the test program is $10,310.

3 - ZEOLITE CHEMICAL HEAT PUMP

3 - ZEOLITE CHEMICAL HEAT PUMPS

3.1 - Zeolite Materials

'Zeolite' is a general term applied to porous, crystalline aluminosilicates. There are seven varieties that occur naturally in deposits of sufficient quantity and quality to be commercially useful.[1] As early as two hundred years ago, naturally occurring zeolites were observed to release water on heating, and to readsorb water when cooled. The ability to selectively adsorb other gas molecules was noted about sixty years ago. The porous crystalline structure, which forms a void with an aperture, was determined by x-ray diffraction analysis about fifty years ago. The seven significant natural zeolites are identified in Table 3.1

Synthetic zeolites were introduced in the 1950s. Natural zeolites have, however, been considered for applications (e.g., as catalysts) where the operating temperature is much higher than that allowed for synthetic zeolites. Also, the lower energy hydration bond with natural zeolites means that approximately reversible thermodynamic cycles may be constructed within a narrower range of temperatures. This could be important when low-grade waste heat is to be utilized.

Natural zeolites are a more variable product than synthetic zeolite and may consist of a mixture of materials rather than a single species. This makes it difficult for a designer to guarantee performance unless he has access to special test data for a prepared product. It is possible that, if the benefits of a lower hydration energy are more widely appreciated, then modified synthetic zeolites patterned after natural zeolites may be more widely marketed. A range of products with different hydration energies would allow the design of zeolite heat pumps that are optimized for the intended application.

A number of synthetic zeolite materials had been developed by 1953. Some of these were selected for their potential value to the chemical

TABLE 3.1

IMPORTANT NATURAL, ZEOLITES

Zeolite	% Water Adsorbed	Aperture, Angstroms	Comments
Analcime	8	2.8	
Chabazite	28	5	(1) A Na-Ca form is available from Nova Scotia - good desiccant properties, rapid reaction rate. (2) Natural Chabazite used at University of Texas and MIT for solar energy studies. (3) Union Carbide have a Chabazite-rich AW-500 product from deposits at Bowie, Arizona. (4) High methane adsorption capacity.
Clinoptilolite	14	3.8	Crushed, screened clinoptilolite reported to be available at a cost of $200-$300/ton, fob minesite, 1976. Mined by Double Eagle Petroleum and Mining Co. at Buckhorn, NM. Reported to by used in pilot scale plants to remove NH_4^+ from wastewater. Projected demand for this application of several hundred thousand tons per year.
Erionite	20	3.0	Unique low enthalpy of water sorption ('Sorption and ion exchange in sedimentary zeolites', D. L. Peterson, F. Helfferich, G. C. Blytas, J. Phys, Chem Solids, 26, 1965, pp 835-848.)
Ferierite	12	5.0	
Mordenite	15	4.2	Used for oxygen extraction from air by pressure swing adsorption. May be synthesized e.g., Zeolon Z200 H.
Phillipsite	22	3.0	

NOTE: The Enthalpy of the condensation reaction of water vapor is less for the natural zeolites than for the synthetic molecular sieve materials, e.g., normal condensation enthalpy to liquid water 2.3 MJ/kg H_2O, on natural zeolite 2.8 MJ/kg H_2O, and as synthetic molecular sieve zeolites 4.2 MJ/kg H_2O. A natural zeolite can be dehydrated with a temperature of 250'C.

industry and developed into commercial products.[2] These were found to be of great benefit as desiccants and selective adsorbers for specific gases. The basic types of Molecular Sieve (i.e., Zeolite) material are listed in Table 3.2. These zeolites differ from the natural zeolites in that the bond with water vapor is more energetic. They are characterized by a crystalline structure that contains a small (0.3 to 0.8 nanometer diameter) void. The properties of both natural and synthetic zeolites may be modified by substituting different atoms in the crystalline structure so that electrical charge distribution is changed.

Continuing research has led to widespread use of modified zeolites as catalysts, particularly for hydrocarbon gas reactions. Reactions may be obtained that are unattainable without the catalyst. A recent (1982) announcement, for example, was the ability to convert methanol to high-octane gasoline in one step over a zeolite type catalyst. Zeolites and their properties were the subject of more than 10 000 patents issued by 1982. Approximately 25 000 technical papers had been published on the subject by 1980.

A recent development[3] has led to the introduction of a new family of molecular sieve materials, some of which are structurally related to zeolites. This new family is based on aluminophosphates, which are crystallized using a range of amine compounds as templates. The new materials will act as drying agents and may be regenerated with less energy than the normal commercial molecular sieve materials. At this time, however, these products are being promoted for catalyst applications.

3.2 - The Use of Zeolite in a Chemical Heat Pump

3.2.1 - Introduction

Zeolites can be used to store energy by way of their tendency to adsorb water (or any polar molecules). The energy can be

TABLE 3.2

COMMERCIALLY AVAILABLE MOLECULAR SIEVES

Type	% Water Adsorbed	Molecular Aperture, Angstroms	Comments
3A	23	3	)
4A	28	4	) Heat of adsorption) 4.2 MJ/kg H_2O
5A	28	5	)
13X	36	10	)

NOTE (1) The above require a temperature of about 300°C to remove the adsorbed water to 10% of the maximum loading at a pressure of 1.0 psi.

(2) Data published by Union Carbide.

recovered from the 'stored' state by an appropriate procedure, as explained a little later. The energy 'storage' is in the form of thermal energy as well as through chemical bonding. The portion which is in the form of thermal energy (based on temperature only) is subject to losses and recovery just as any other inert thermal storage system. The portion which is stored in the chemical bonds can be recovered at a temperature which is independent of the conditions under which it was stored, but dependent only on the conditions under which it is recovered. It is this chemical bond reversal procedure which permit zeolites to be used as the transfer or pumping agent in chemical heat pumps.

Unlike some other chemical heat pump compounds, the common form of zeolites is a solid, which may be in a powder or small pellet form. For the purposes of this study, it is assumed that the zeolite is in a pellet form which permits air or a mixture of air and water vapor to move through a bed of it without moving solid material, and with relatively little pressure loss in the flow.

3.2.2 - Principle of Zeolite Heat Pumping

The high potential energy form of zeolite corresponds to low adsorbed water content, and vice versa. Therefore, to increase this stored energy in zeolite requires that the adsorbed water content be reduced. This may be accomplished by passing an air flow through the zeolite bed which is at a high temperature and at a humidity level which is lower than the equilibrium vapor pressure for the temperature and state of sorption of the zeolite. This air flow raises the zeolite temperature, causing it to release some of its water content in order to approach equilibrium with its surroundings. This water vapor which is released is carried out with the air stream. The enthalpy of vaporization accounts for a substantial fraction of the energy contained in the exhaust flow during the drying (charging of the

bed) process. If it can be usefully recovered, the efficiency of the charging process is significantly improved.
To recover the potential energy of the zeolite bed, humid air can be passed through it. If the humidity level of the air passing through the bed is higher than the equilibrium value for the zeolite at its temperature and state of sorption, the zeolite will adsorb water from the air stream and release the corresponding energy of adsorption. This energy release causes the bed temperature to rise, which causes heat to be transferred to the air stream. The air stream, therefore, enters the bed at a given temperature and humidity level and leaves at a higher temperature and lower humidity level.

3.2.3 - Practical Application of Zeolite to Heat Pumping Processes

In the case of an open cycle type of system such as that chosen for the Sodium Hydroxide Chemical heat pump phase 'A' study, a somewhat different approach would be required. The regeneration phase using externally supplied heat would remain, but the condensate would not be collected. Regeneration heat recovery would boost the efficiency of the system. The adsorbing (heating) cycle would make use of the moisture in the warm wet air stream from the dryer as described in the Phase 'A' study. The air would enter the regenerated zeolite bed where its moisture content would be reduced and its temperature increased before being returned to the dryer.

The simplest mode in which to employ zeolite for the purpose of heat pumping is to alternately charge and discharge the bed. This can be done as in Figure 3.1 where two beds are shown to be used alternately to allow continuous operation. The switching valves direct the flow so that while one module is being charged (dried), the other is being discharged. The major disadvantage of this approach is that the outlet conditions will vary quite

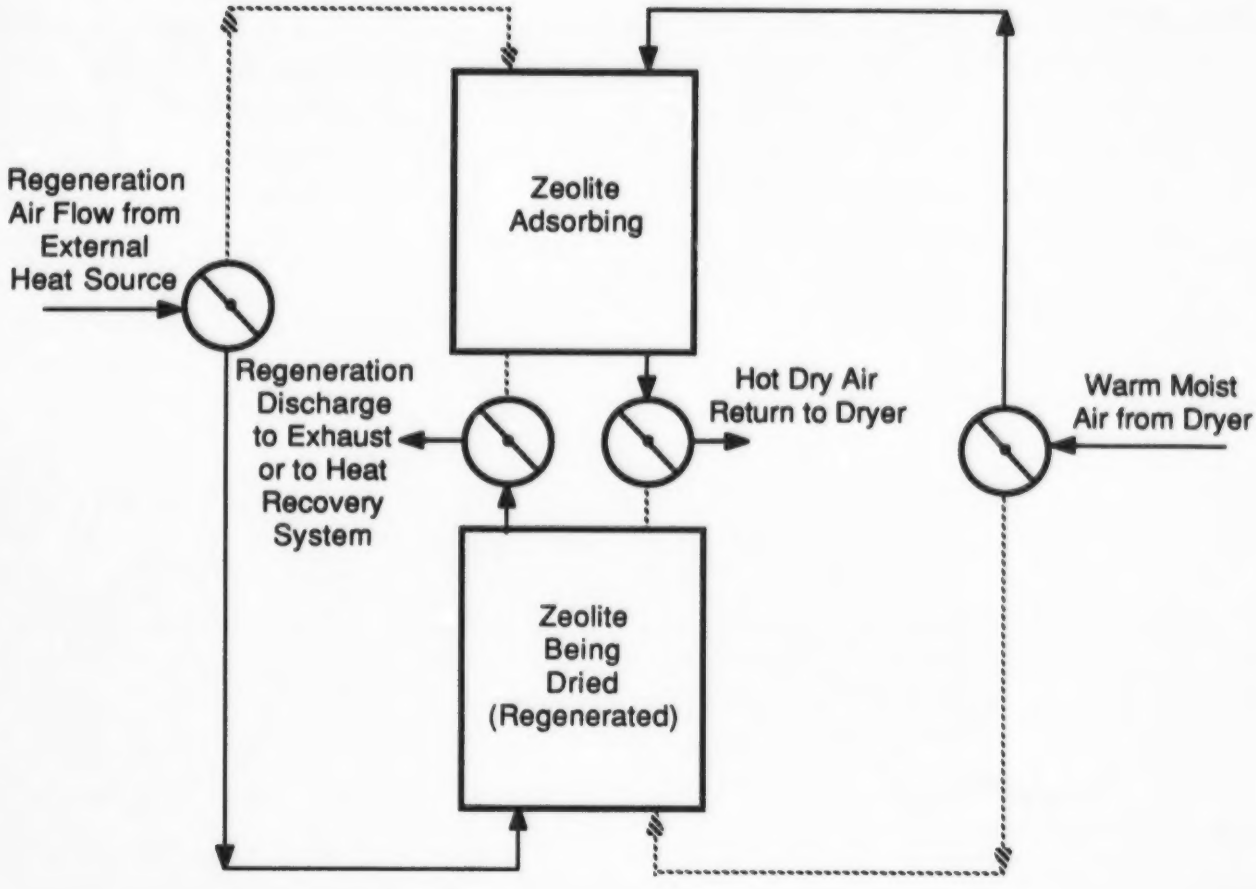


Figure 3.1

Tne Evaluation of Zeolite and
Sodium Hydroxide Chemical Heat Pumps

Alternating Zeolite Beds Used for Heat Pumping

considerably with time, if only one pair of bed is used for the operation. This disadvantage can be overcome by adding more beds in series, so that, with appropriate controls or choice of operating conditions, the exhaust flow can be made quite uniform in time. The added advantage with this approach is that the charging process can also be made more efficient, since it too can be controlled to ensure more complete depletion of the energy of the air flow used to charge the beds. A disadvantage is that the control of the operation of the system becomes more complex.

Another operation which might prove more satisfactory is to adopt a rotating cylinder geometry, much as thermal wheels are used in some HVAC applications and rotary regenerative heaters recover heat in power generation plant combustion air systems. In effect this is a multiple cell heat exchanger with each cell being alternately charged and discharged as it rotates to the appropriate flow path. With appropriate design, the outlet conditions could be made to be uniform in time, as the rotating bed is alternately charged on one side while being discharged on the other. Optimum performance could be achieved by several passes through the wheel at successive circumferential locations, much as the multiple fixed bed arrangement can be used to improve the overall efficiency. Figure 3.2 shows how this might be accomplished with a single pass for the charging flow and another single pass for the discharging flow.

3.3 - Review of Published Technical Data

The purpose of the review was to identify and evaluate technical publications proposing the use of zeolite for upgrading waste heat in a heat pump system. This information was then to be used to make a comparison between the potential benefits of sodium hydroxide and Zeolite based heat pumps. It is not within the scope of this study to carry out any further investigations into other forms of chemical heat pumps nor to make any detailed comparisons between them.

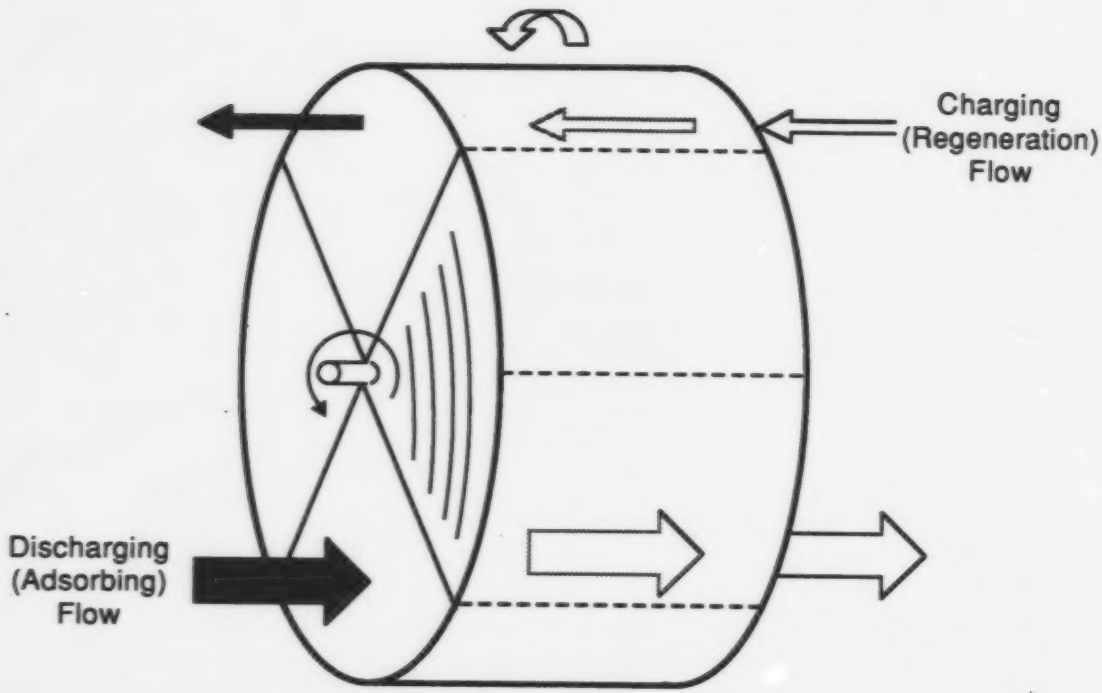


Figure 3.2

The Evaluation of Zeolite and
Sodium Hydroxide Chemical Heat Pumps

Zeolite Thermal Wheel

A literature search revealed that many papers have been published on the application of zeolites to thermal systems. Most of the recent research activities appear to be related to the use of zeolite as a heat storage medium, in many cases using solar heating as the heat source. Also, the use of zeolites has been investigated for use in refrigeration cycles, associated with solar energy in most cases. A number of publications [4], [5], [6], [7], [8], [9], [10], [11], [12], [13], give some insight into the work on solar energy and refrigeration applications of zeolite. A good overview of the worldwide status and state-of-the-art of chemical heat pump systems was provided at the end of 1983.[14] This identified ten major systems/concepts that had been previously developed or showed significant promise for future development, and listed all the current reported work. These included lithium bromide/water, sulphuric acid/water, sodium hydroxide/water and zeolite/water systems among others.

The only reported work on zeolite/water heat pump systems was in West Germany, the organizations/researchers being the University of Munich, TU Munchen, and AEG. It was only possible to identify technical publications by the University of Munich.[15], [16], [17] Their work at that time was well advanced and several laboratory test model systems had been built, the largest containing 800 kg of zeolite.

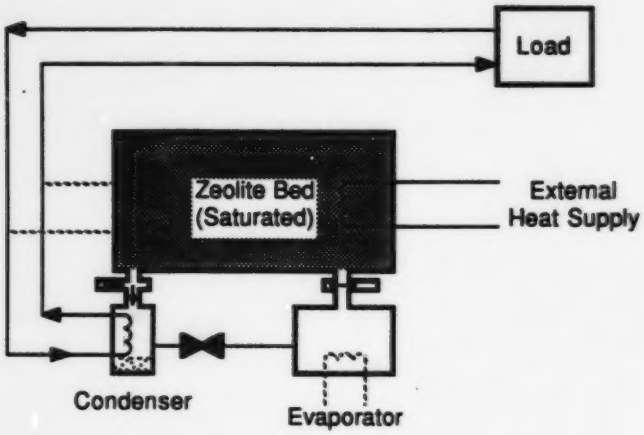
The University of Munich approach had a different starting point than other zeolite applications, being aimed at uses other than solar powered systems. Such applications using solar heating in the regions of up to 100°C place zeolite systems in competition with several other solid or liquid sorption systems. It is possible that the zeolite systems may not be as cost effective as these other systems in those circumstances. The University of Munich team recognized the fact that the zeolite/water system is capable of operating at higher temperatures and therefore has the potential for upgrading industrial waste heat. It is basically a sorption heat pump in which the sorption medium is a solid adsorber rather than a liquid. The operating phases of their heat pump are shown in Figure 3.3. The system configuration used is a closed system operating in a vacuum, although an open system

configuration could equally be used, as described later. As shown in Figure 3.3(a) external heat is supplied to drive the moisture out of the Zeolite during the regeneration or desorption phase of operation. The moisture is driven off as steam and passes to the condenser where it liquifies by heat exchange with the cool flow returning from the load. The load would be any system which could accept the heat from the heat pump for useful purposes, such as a domestic central heating system or industrial process. This method of operation together with the cooling phase which follows, enables a significant portion of the heat required to regenerate the Zeolite to be recovered.

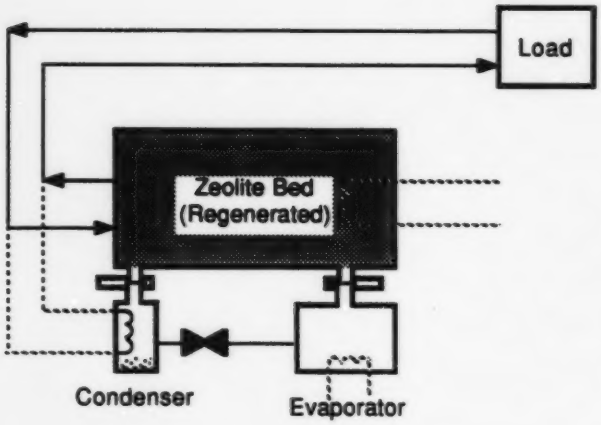
The desorption phase is followed by the cooling phase, Figure 3.3(b) in which most of the heat remaining in the Zeolite after regeneration is extracted by the load. With falling temperatures in the Zeolite, the vapor pressure decreases.

When the vapor pressure has fallen below the evaporator pressure the adsorption can start, Figure 3.3(c). The liquid in the condenser is allowed to flow into the evaporator, and heat exchange with the atmosphere provides a heat source which evaporates the liquid in the evaporator. The Zeolite rapidly adsorbs the water vapor and heats up. The heat of adsorption is then available for supplying the load, and the adsorption process continues until the vapor pressure in the Zeolite has reached the vapor pressure of the evaporator.

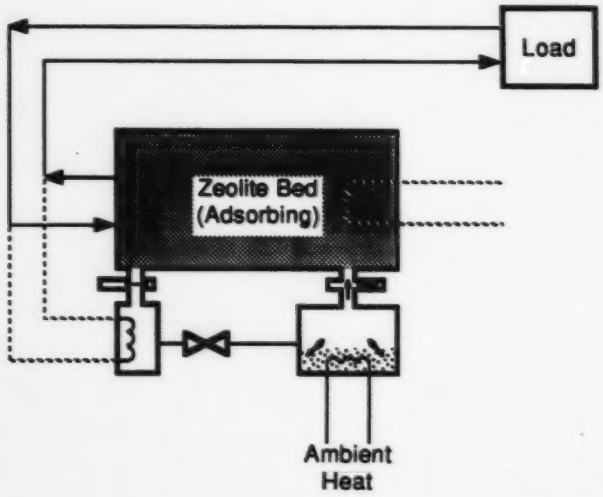
The operation of the adsorption process is mainly dependant upon the pressure difference between the evaporator and the Zeolite. Thus adsorption starts if the evaporator pressure increases due to lowering of zeolite temperatures by heat exchange with the load.



(a) Desorption (Regeneration)



(b) Cooling



(c) Adsorption

Figure 3.3

The Evaluation of Zeolite and
Sodium Hydroxide Chemical Heat Pumps

Closed Cycle Zeolite Heat Pump

3.4 - Performance of a Zeolite Heat Pump and Comparison with the Sodium Hydroxide System

In order to compare the performance of zeolite and sodium hydroxide chemical heat pumps, bearing in mind there are many possible applications that could be chosen, it was decided to compare on the basis of a paper drier. More specifically the comparison was made using the 1/2% scale paper drier proposed in the Phase 'A' study. In this manner, the results from the Phase 'A' calculations could be utilized to compare the systems in the context of a potential industrial application.

It was originally intended that a complete heat balance evaluation and comparison would be attempted, but due to limiting budget constraints this was not possible. The comparison was therefore carried out on the basis of the approximate size and type of zeolite heat pump required for the same duty as that which formed the basis for sizing the N_aOH heat pump.

3.4.1 - Performance of a Zeolite Heat Pump

The performance of a rotating wheel zeolite heat pump can be simulated with an extension of the model developed in earlier work for the NRC.[18] It is modelled as a packed bed through which a gas flows, exchanging heat and mass (water) between the solid zeolite particles and the gaseous flow. For this application, the bed is a short cylinder with axial flow between an inner radius and an outer radius. The bed is allowed to turn slowly, so that new supply of charged zeolite is exposed to the flow to be dehydrated and heated. This takes place on one side of the cylindrical face while the other side is subjected to a flow of dry, high temperature air which removes some of the water and leaves the bed in a relatively more charged (dry) state.

The extended model has been coded for the computer, and preliminary results support the concept. In the following section, an approximate design of the wheel is given.

3.4.2 - First Order Zeolite Wheel Design

In the bench scale N_aOH heat pump to be used for simulated paper drying, 0.796 kg/s of air containing 0.122 kg/s water vapor enters the contacting tower at 77°C, and 0.796 kg/s air and 0.089 kg/s water vapor emerge at 106°C. For the air and the portion of water vapor which recirculates back to the dryer this corresponds to an energy increase in this flow of approximately 106,251 kJ/h. With a zeolite adsorption energy release of approximately 3953 kJ/kg of water, this would require a water adsorption rate of 26.88 kg/h, if a zeolite bed was used to provide the energy.

In the N_aOH system, almost 120 kg/h of water is removed from the flow. Making this a criteria, and planning to take the zeolite from 0.12 to 0.22 kg water per kilogram of zeolite in a cycle, this would require the gas flow to be exposed to approximately 1200 kg/h of zeolite in the state of having
0.12 kg water per kg of zeolite.

If the zeolite wheel is allowed to provide this requirement, the dimensions and the rate of revolution need to be chosen to best meet this demand. In principle, any combination of parameters which produce this zeolite mass rate will suffice. In practice, there will be a range of sizes which will best serve the requirement. The first order design is not an optimized specification, but will meet the requirement.

The sizes selected for this first order design are as follows.

Wheel outer diameter:	0.91 m (3.0 ft)
Wheel inner diameter:	0.305 m(1.0 ft)
Wheel thickness:	1.83 m (6.0 ft)
Zeolite density:	64 kg/m^3 (4 lb/ft^3)
Wheel revolution rate:	13.65 rad/h.

These sizes will provide the rate of moisture removal, as with the N_aOH absorber, but will raise the temperature of the flow to a higher level than did the N_aOH system. Since each system is different, each individual design will need to be examined as to the most important variables to be established, and the design assembled around that.

3.4.3 - Results for the First Order Design

The computer program has been modified to run for the condition noted .

Inlet Flow	0.796 kg/s air 0.122 kg/s water vapor at 77°C
Wheel	As for the First Order Design Initially at 77°C
Zeolite	Union Carbide Type 13X Initially at 12% moisture

The graph in Figure 3.4 shows the air temperature out of the wheel as it varies with time, for the case with the wheel turning at a fixed speed. The initial and final moisture content selected for the Zeolite is worthy of further discussion. Zeolite will obviously only adsorb water up to a certain limit, and it is also very difficult to deplete all the water from the zeolite. For type 13X for example, the maximum adsorption is about 33% by weight. Experience has shown that because the rates of achieving the maximum water content are much slower than achieving 22 to 25% adsorption by weight, preliminary design for a system is made on the basis of achieving a 22% water content. Then, if the dynamics of the system are favorable, we achieve more than the preliminary design projected, as is the case in the

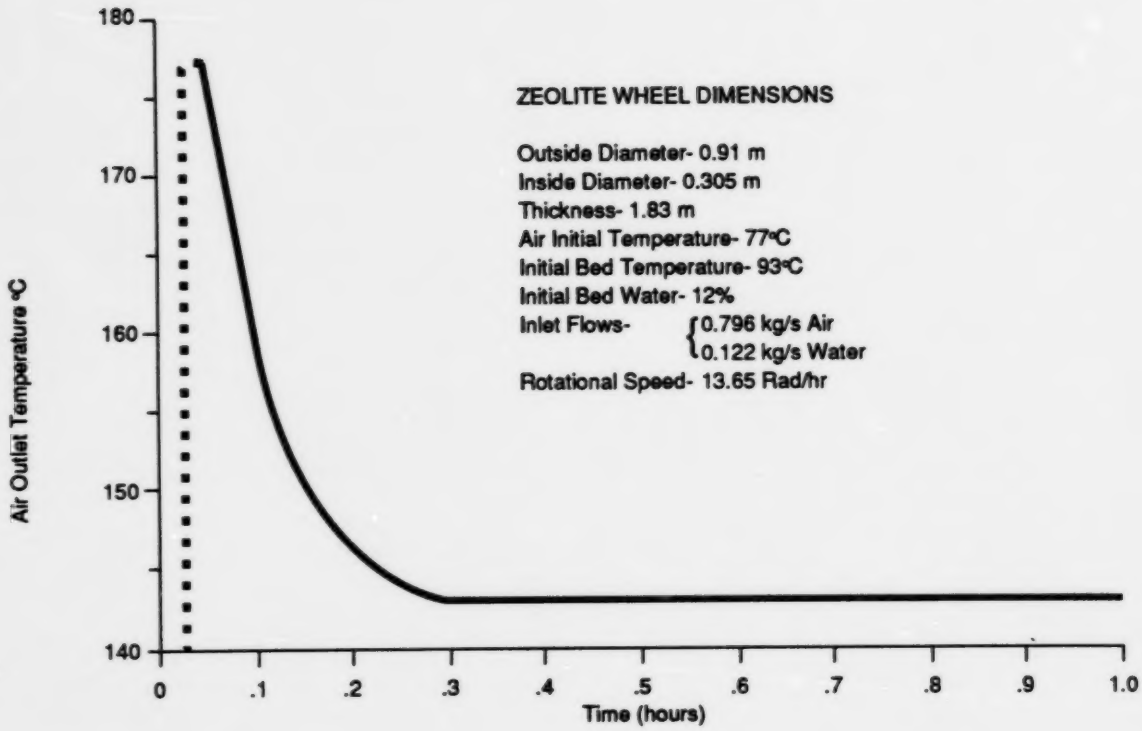


Figure 3.4

The Evaluation of Zeolite and
Sodium Hydroxide Chemical Heat Pumps

Zeolite Wheel Outlet Air Temperature Variation with Time

the present simulation. Similarly, for the easily achieved water vapor pressures (without using artificial means to deplete them) it is reasonable to expect the lower limit of the water content to be about 12% during the regeneration process, when modest temperatures are used for the process. The range from 12 to 22% is not necessarily limiting, but is a good basis from which to do a first order design, based on experience.

3.4.4 - Comparison with the N_aOH System

The dimensions of the contacting tower for the N_aOH system 1/2% scale model in the Phase 'A' study was 0.398 m^2 cross-sectional area and 3.41 m high. This corresponds to a tower diameter of 0.71 m.

Based on the first order zeolite wheel design calculations, the equivalent zeolite system would be 0.91 m diameter and 1.83 m long.

The maximum operating temperature of both the zeolite and N_aOH systems have yet to be established. The temperature used for the N_aOH system drier application in the Phase 'A' study was 107°C, based on process conditions, and to some extent on concentration levels of N_aOH/H_2O which seemed manageable. The upper limits may be investigated as part of a research and development program. Zeolites are capable of operating at relatively higher temperatures, and the molecular sieve Type 13X selected for the zeolite heat pump can withstand 340°C and possibly higher. The water adsorption capacity however falls as operating temperature increases, being about 20% at 250°C of the capacity at 100°C.

There are significant differences in the regeneration cycle of the two systems. The N_aOH system required only low temperatures for regeneration and the use of low grade waste heat is a

possibility. On the other hand, zeolite can be regenerated at high temperature (typically up to 300°C) or lower temperatures, depending upon the operating parameters of the system. It has been shown that 200°C is, in many instances, adequate for regeneration purposes, and in some cases 100°C is sufficient. However, NaOH probably can be considered as requiring, generally, lower temperatures for regeneration.

To carry out a detailed heat balance analysis and comparison of the Zeolite and N_aOH systems requires that the rotating wheel concept (or other alternative) be further developed and the N_aOH model testing be completed, before a more definitive comparison can be made.

3.4.5 - Relative Advantages/Disadvantages of Zeolite and N_aOH Systems

At the present stage of development it is only possible to make generalized comments on relative advantages and disadvantages of the two chemical heat pump systems. It is emphasized that at this point in time there are no apparent factors which would eliminate one or the other from future consideration.

A comparison is as follows.

Mechanical Complexity

Basically, the N_aOH system is more complex in that it requires a number of different components in order to build a functional system. These include typically

- contacting tower (absorber)
- demister
- evaporator (regenerator)
- transfer pump
- recirculation pump

- desuperheater/condenser
- air/water separation with vacuum and drain pumps
- flow control valves
- interconnecting piping
- cooling water supply.

The zeolite system has much fewer types of components and is a single-fluid system, air being used as both the interfacing fluid with the paper drier and the regeneration heat transfer medium. The basic components envisaged for a zeolite heat pump would be

- zeolite beds (such as thermal wheels or zeolite vessels)

- regeneration heaters (which maybe integral with the zeolite container or separate in the heat wheel design)

- heat exchangers for recovery of regeneration heat

- control dampers for direction of air flow around the systems.

However, in order to provide an air flow to the drier at a fairly uniform temperature it will be necessary to provide a multiplicity of zeolite vessels which will operate at varying stages of charge/discharge. The alternative would be the thermal wheel system which may need to be more than one wheel in an industrial scale unit. The ducting and damper arrangements would probably be quite complex because of the combinations of thermal wheels or zeolite vessels and heat exchangers required.

In summary, it appears that whilst the zeolite system may be fundamentally simpler than the N_aOH system, it may transpire that this is not the case in a full scale application. The N_aOH system has few moving parts whereas the thermal wheel zeolite option would be a rotating device with dynamic seals.

Complexity of Control

The N_aOH system is relatively simple to control, being essentially a steady state device with control required only to correct minor perturbations in continuous operation and to maintain N_aOH inventory control.

The zeolite system on the other hand is likely to need a complex control system to allow for the discontinuous and varying performance of each of the zeolite beds, in order to provide a steady heat flow to the drier. This may be alleviated to some extent if the thermal wheel can be applied effectively with a limited number of units.

Materials of Construction

The materials of construction for certain components of the N_aOH system (i.e., the absorber, piping and the tube-side of the evaporator) require further investigation in order to minimize the capital cost. The materials to be used for contact with N_aOH remain under investigation.

In the case of the zeolite system, materials of construction should pose far fewer questions because the zeolite is essentially a non-toxic and barely corrosive material. Care will need to be taken with regard to sealing at the high temperatures experienced during regeneration. Sealing is one of the greatest problem associated with rotary regenerative (thermal wheel) type heat transfer devices in power generation plant, where considerable maintenance and adjustment of the axial and radial stainless steel flexible seals is required.

In general, however, the zeolite system should have fewer materials related concerns than the N_aOH system.

4 - RECOMMENDATIONS & CONCLUSIONS

4 - COMPARISON OF SODIUM HYDROXIDE AND ZEOLITE CHEMICAL HEAT PUMP

4 - RECOMMENDATIONS & CONCLUSIONS

4.1 - Recommendations

The primary research and development activities identified for the N_aOH system are the laboratory scale contacting tower and the associated test program, which form Sections 2.2 and 2.3 of this report.

The basic purpose of this program is to confirm and refine the analytical design methods for the contacting tower.

The model testing could however be extended to cover a number of other factors requiring investigation. These would include

- materials testing to evaluate various potential materials of construction. These would predominantly be plastics, fibre reinforced plastics, lined plastics etc. to try to find durable cost-saving alternatives to expensive metals and alloys

- the temperature level of 107°C selected for the Phase 'A' drier application was to meet process conditions and to use concentration levels of N_aOH/H_2O which seemed manageable without further research. The sodium hydroxide concentration in the working fluid should be reduced slightly, in order to prevent solidification of the working fluid in storage vessels and transfer lines during startup or shut down operations. A 60 wt% solution becomes unstable at about 53°C, where as a 50 wt% solution becomes unstable at about 10°C. While a 60 wt% solution may be appropriate for the proposed drying operation where the ambient temperature is high, the concentration of sodium hydroxide in the working fluid should be selected so that solidification cannot occur under the anticipated ambient conditions. Otherwise the metastability of concentrated solutions at ambient conditions would have to be verified. For the laboratory trials a maximum concentration of 53 wt% is recommended.

The coincident reduction in fluid viscosity would facilitate mass and energy transfer and fluid circulation.

- The calculations carried out for the zeolite system were used to compare the approximate size of a zeolite heat pump with that of the N_aOH system. Due to budget limitations they did not, however, enable a heat balance to be prepared, accounting for recovery of at least some of the heat of regeneration, for a complete performance comparison with the N_aOH system. Also, although the concept of a thermal wheel for practical application of the zeolite system appears a sound proposition, it requires further verification before it can be confidently applied. It is recommended that a small laboratory scale model be built to test the concept of the thermal wheel and confirm the temperature variations with speed of rotation and concurrent partial regeneration. It could presumably be designed in such a way that it could also operate in a static mode. The calculational computer code should be refined and verified against the laboratory scale model. A full simulation of the entire process, including both the adsorption and regeneration phases, should be carried out.

- Investigation into performance at lower regeneration temperatures should be incorporated into the test program and simulation.

4.2 - Conclusions

- Both the Sodium Hydroxide and Zeolite chemical heat pump concepts are technically feasible but more data is required to carry out detailed economic comparisons.

- It appears likely that due to conservations in the original calculations, the NaOH system can be made smaller than originally envisaged.

- The rejection of either system at this time would be unfounded.

- Final model testing is needed for the NaOH system, and further model testing and analytical work is needed for the realization of the Zeolite wheel heat pump concept.

- At this point it appears that the Zeolite heat pump may be capable of operating at higher temperatures than the NaOH heat pump.

- A major concern over the NaOH system is the need for proving of cheaper materials of construction in order to enhance the economic viability of the system.

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APPENDIX A

POTENTIAL APPLICATIONS

APPENDIX A

POTENTIAL APPLICATIONS

Drying Processes

A recent study[1] was carried out for the Canadian Electrical Association on the subject of "The Potential for Electrical Drying Processes in Canadian Industry".

The study included a survey of industrial drying processes in current use in Canadian industry, obtained by the completion of questionnaires by responding companies. One hundred and thirty (130) provided complete details of their drying processes, which were then matched with appropriate drying electrotechnologies. In particular, many were matched with heat pumps, which could be chemical heat pumps of the sodium hydroxide and zeolite types. In addition, some higher temperature processes could also probably be satisfied by chemical heat pumps. Rather than trying to match the processes with an upper temperature selected somewhat arbitrarily as the ultimate development limit for the chemical heat pumps, it was decided to show details of all the processes identified. Tables A.1 to A.6 repeat the details shown in the drying report, from which it can be seen that there is considerable scope for evaluation of potential applications for chemical heat pumps in industrial drying processes.

TABLE A.1

INDUSTRY: NON-METALLIC MINERALS AND PRODUCTS

Drying* Temperature or Range	Product Temperature Limit*	Product or* Process
170°C	790°C	Potash Crystals 60% K_2O
200°C	790°C	Potash Crystals 62% K_2O
230°C	790°C	Potash Crystals <100 ppm Na
200°C	790°C	Compacted Potash Product
0° to 210°F	-	Sodium Sulphate Na_2SO4
450°F	400°F	Potash 3% and 5%
1800°F	1500°F	Asbestos Fibres and Stone
400°F	1400°F	Potassium Chloride (KCl) Crystals
230°F	1400°F	KCl Granulated
200 to 300°C Binder	300°C	Fiberglass Wool &
900 to 250°F	-	Asbestos Mineral
265°F	280°F	Fiberglass Strands in Round Packages
350 to 690°F	700°F	Fiberglass Strands in Sheets
630°F	680°F	Coated Glass Strands
300°C	75°C	Limestone and Shale
400°F	450°F	Calcium Silica Pipe Insulation

*Identified in questionnaire reply.

TABLE A.2

INDUSTRY: CHEMICALS AND CHEMICAL PRODUCTS

Drying* Temperature or Range	Product Temperature Limit*	Product or* Process
85°C	75°C	Calcium Hypochlorite $Ca(ClO)_2$
110°C	None	Sodium Chlorate $NaClO_3$
400 to 600°F	600°F	Coke
500°C	600°C	Breeze Coke
120°C	125°C	Pentaerythritol $C(CH_2OH)_4$
60 to 105°C	110°C	Cellulose Acetate Filaments and Granules
235°C	235°C	Nylon
105°C	115°C	Polyethylene
72 to 100°F	130°F	Raw Cell Batteries
360°C	-	Ammonium Nitrate NH_4NO_3 (Liquid)
300°F	-	NH_4O_3 (Granules)
265°F	-	Urea
300°F	-	Dicyanamide
1000°F	-	Calcium Phosphate
150 to 250°F	-	Catalyst
360°F	-	Hydrogen Cyanamide

*Identified in questionnaire reply.

TABLE A.2 - 2

INDUSTRY: CHEMICALS AND CHEMICAL PRODUCTS

Drying* Temperature or Range	Product Temperature Limit*	Product or* Process
345°F	450°F	Ammonium Nitrate
350°F	450°F	Urea
190°F	200°F	Ammonium Phosphate
250°F	-	Nickel Powder
160 to 190°F	-	Ammonium Sulphate
110 to 210°F	115°F	Urea
110°F	120°F	Nickel Coinage Blanks
135 to 145°F	150°F	NBS Coinage Blanks
200°F	500°F	Cobalt Powder
30 to 115°C	28 to 77°C	Ammonium Nitrate
200°F	-	Ammonium Nitrate
1000°F	250°F	Coke
250 to 300°F	220°F	$CaCO_3$ Mixture

*Identified in questionnaire reply.

TABLE A.3

INDUSTRY: METALLIC MINERALS

Drying* Temperature or Range	Product Temperature Limit*	Product or* Process
1300 to 1600°F	140°F	Copper Concentrate
1300 to 1600°F	140°F	Zinc Concentrate
380 to 2200°F	470°F	Copper Concentrate
180 to 1200°F	400°F	Molybdenum Concentrate
320°C	70°C	Copper Concentrate
320°C	70°C	Silica Flux
160 to 180°C	2800°C	Uranium Yellow Cake
150 to 1200°C	200°C	Copper and Zinc Concentrate
127 to 144°C	150°C	Ammonium Diuranate
288 to 404°C	500°C	Uranium Fluoride UF_4
300 to 1800°F	-	Copper Concentrate
300 to 1800°C	-	Lead/Copper Concentrate
300 to 1800°F	-	Zinc Concentrate
1600 to 2000°F	-	Lead Bulk
1600 to 2000°F	-	Zinc

*Identified in questionnaire reply.

TABLE A.4

INDUSTRY: TEXTILES, RUBBER AND PLASTICS, METAL PRODUCTS

Drying* Temperature or Range	Product Temperature Limit*	Product or* Process
250 to 350°F	350°F	Carpet
200 to 225°F	250°F	Dyed Yarn Skeins
200 to 250°F	300°F	Dyed Carpet
225 to 300°F	300°F	Latex on Carpet
180°F	200°F	Food Casings
150 to 275°F	180 to 300°F	Paint
150 to 350°C	150 to 300°F	Paint
200°F	120°F	Steel
130 to 150°F	-	Polyethylene Granules
140°F	-	PVC Granules
325°F	600°F	Steel
400°F	400°F	Paint
800°F	160°F	Steel (Water)
350°F	65 to 80°F	Steel (Paint)

*Identified in questionnaire reply.

TABLE A.5

INDUSTRY: WOOD PRODUCTS, PULP AND PAPER

Drying* Temperature or Range	Product Temperature Limit*	Product or* Process
400°F	450°F	Veneer
200°F	450°F	Wood
250 to 350°C	170°C	Wood
255 to 285°F	-	Wood
160 to 180°F	250°F	Plywood Veneer
330 to 370°F	400°F	Wood
220°F	240°F	Wood
300 to 500°C	50 to 100°C	Sawdust
170 to 225°F	400°F	Newsprint
180°F	240°F	Newsprint
138°C	214°C	Pulp
250°F	-	Fine Papers
200 to 400°F	130°F	Wood Bark
300 to 475°F	480°F	Molded Pulp
270 to 300°F	135°F	Pulp
140°F	-	Cartons
175 to 268°F	454°F	Pulp
220 to 320°F	350°F	Board

*Identified in questionnaire reply.

TABLE A.5 - 2

INDUSTRY: WOOD PRODUCTS, PULP AND PAPER

Drying* Temperature or Range	Product Temperature Limit*	Product or* Process
250 to 290°F	250°F	Newsprint
220 to 550°F	600°F	Wood Residue
190°C	100°C	Spent Sulphite Liquor
370 to 390°C	150°C	Container Board
93°C	182°C	Pulp
1000°F(I.R.)	250°F	Unspecified Papers
280 to 600°F	180°F	Unspecified Papers
220 to 240°F	212°F	Newsprint
290 to 330°F	-	Tissue

*Identified in questionnaire reply.

TABLE A.6

INDUSTRY: FOOD PRODUCTS, BEVERAGES AND GRAINS

Drying* Temperature or Range	Product Temperature Limit*	Product or* Process
40 to 80°c	90°C	Wheat
120 to 160°C	200°C	Biscuit
150°C	180°C	Biscuit
120 to 180°C	200°C	Cereal
220 to 280°C	300°C	Flaked Grain
100 to 120°C	150°C	Flaked Grain
220°F	-	Flour
190°F	90°F	Grain
350°F	350°F	Biscuit
300°F	250°F	Oats
300 to 350°F	110°F	Puffed Wheat and Rice
400 to 450°F	350 to 450°F	Animal Food
150 to 195°F	195°F	Malt
60 to 85°C	85°C	Wet Grain
200°F	90°F	Grain
220 to 265°F	250 to 275°F	Meat Products, Cooking Oil
350°F	95°F	Coffee
410°F	175°F	Dream Whip

*Identified in questionnaire reply.

TABLE A.6 - 2

INDUSTRY: FOOD PRODUCTS, BEVERAGES AND GRAINS

Drying* Temperature or Range	Product Temperature Limit*	Product or* Process
140 to 230°F	86 to 100°F	French Fries
300°F	110°F	Gluten
350°F	110°F	Starch
172°F	125 to 140°F	Whey
360 to 375°F	125 to 140°F	Whey
310 to 325°F	140 to 150°F	Cheese Powder
200 to 400°F	300 to 400°F	Bread
400°F	150°F	Starch
450°F	150°F	Gluten
250°F	150°F	Tobacco
150 to 285°C	300°C	Tobacco
80°C	38°C	Sugar
85 to 130°C	130°C	Liquid Sugar
300 to 400°F	-	Bottles
230°F	250°F	Spent Grain
290 to 350°F	350°F	Yeast
230°F	200°F	Fruit Juice
150 to 212°F	200°F	Stillage

*Identified in questionnaire reply.

TABLE A.6 - 3

INDUSTRY: FOOD PRODUCTS, BEVERAGES AND GRAINS

Drying* Temperature or Range	Product Temperature Limit*	Product or* Process
200 to 300°F	250°F	Grain
90 to 670°C	90°C	Grain
60 to 110°C	90°C	Stillage

*Identified in questionnaire reply.

APPENDIX B

REVIEW OF PHASE 'A' STUDY

APPENDIX B

SODIUM HYDROXIDE CHEMICAL HEAT PUMP - A REVIEW OF THE PHASE A STUDY INCLUDING A REVISED LABORATORY SCALE TEST APPARATUS

PREPARED BY:

PROFESSOR J. M. SHAW

DEPARTMENT OF CHEMICAL ENGINEERING
AND APPLIED CHEMISTRY
UNIVERSITY OF TORONTO

1987/05/26

Table of Contents

1. Summary 1

2. A Review of the Phase A Study
   2.1 Summary 2
   2.2 The Number of Mass Transfer Units Required for the Sample Dryer Application 2
   2.3 Mass and Energy Balances 3
   2.4 Height of a Transfer Unit 4
   2.5 Materials of Construction 5
   2.6 Conclusions 6
   2.7 Recommendations 6

3. Proposed Laboratory Scale Absorber Apparatus
   3.1 Summary 7
   3.2 Apparatus Design 7
      a) Apparatus Description 7
      b) Apparatus Specifications 8
      c) Equipment Costs 9
      d) Operating Costs 9

4. Nomenclature 11

5. References 11

1. Summary

On April 7, 1987, ACRES INTERNATIONAL LTD requested a review of a contactor/absorber design for a sodium hydroxide chemical heat pump contained in a report entitled "Chemical Heat Pump Phase A Study" - DSS FILE No. 24SR.31025-4-3015X. Assistance concerning the possible development and operation of a laboratory scale process model was solicited concurrently. This work was initiated pursuant to a meeting on April 16, 1987, and the findings are presented in this report.

Only one transfer unit can be realised in the cocurrent contactor/absorber proposed in the Phase A Study. While this design is adequate for the cited paper drying application (less than one transfer unit is required), it would be more appropriate to operate the contactor/absorber countercurrently, as other applications may require a greater number of transfer units. However, there is essentially no difference between cocurrent and countercurrent operation if only one transfer unit is required.

Little information is presented in the Phase A Study concerning possible or probable controlling steps in the absorption of water vapour by concentrated sodium hydroxide solutions. Consequently, the possible bounds on the required packing depth are broad. The required packing depth for the proposed paper drying application is likely to fall between 0.3 and 1.5 m, depending on the type of packing selected and the operating conditions. A better estimate can only be determined experimentally.

A design for a fully-instrumented, semi-batch, laboratory-scale model of the contactor/absorber is proposed. The proposed design provides a partial simulation of the drying circuit, at a scale which facilitates scale-up. Preliminary cost estimates have been included, based on equipment purchase. Significant cost savings may accrue if equipment can be leased. The estimates include instrumentation and overhead costs. As the cost of instrumentation greatly exceeds previous estimates two analytical alternatives are presented.

2 A Review of the "Phase A Design Study"

2.1 Summary

As indicated in the introduction, this review is restricted to an evaluation of the proposed absorber design. The absorber design proposed in the Phase A Design Study is flawed, as there appears to be some confusion on the part of the authors concerning the equivalence of countercurrent and cocurrent absorption processes. The principal difference between the two types of processes is that in a cocurrent process only one transfer unit can be realised, where as in a countercurrent process any number of transfer units can be realised, with few restrictions. The operation of the two types of processes can only be equated in the special single transfer unit case. Otherwise, different governing equations are employed. The reader is referred to King and Treybal for a more detailed discussion of these matters. For the sample paper drying application cited in the report, only one transfer unit is required and either a cocurrent or countercurrent absorber can be employed. However, there may well be other applications where more than one transfer unit is required, and a countercurrent absorber design would be more generally applicable.

The calculations presented in this section relate to the cited dryer example. Equations are provided where appropriate to facilitate calculations in subsequent stages of the project.

2.2 The Number of Transfer Units Required for the Sample Dryer Application (see Treybal chapter 8 or any other standard text)

The number of transfer units, N_{tog}, under counter current operation, can be expressed as

$$N_{tog} = \int_{Y_2}^{Y_1} \partial Y/(Y-Y^*) + 0.5 \ln[(1+Y_2)/(1+Y_1)]$$

where - Y_1 and Y_2 are the moisture mole fractions in the gas phase at the inlet and outlet conditions respectively
- Y^* is the equilibrium composition

Using the data provided in the report, and assuming that the difference

between the gas composition and the associated equilibrium composition vary linearly over the length of the column,

$$Y^*_2 = 0.036 \quad Y_2 > 0.125 \quad Y^*_1 = 0.154 \quad Y_1 = 0.198$$

yields

$N_{tog} < 1.0$

The above approach is only valid if there is more than one theoretical mass transfer unit. For the single transfer unit case:

$$N_{tog} = (Y_2 - Y_1)/(Y^*_2 - Y_1)$$

$$Y^*_2 = 0.15 \quad Y_2 = 0.153 \quad Y_1 = 0.198$$

$N_{tog} \sim 0.95$

and not 3 as indicated in the report.

2.3 Mass and Energy Balances

Overall mass and energy balances are computed with reference to figure 1, and the mass and energy balance equations. The desired inlet and outlet conditions are specified in the report.

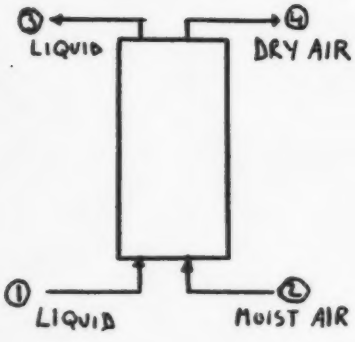

Figure 1

Mass Balances

water $F_1 w_{w1} + F_2 w_{w2} = F_3 w_{w3} + F_4 w_{w4}$

air $F_2(1-w_{w2}) = F_4(1-w_{w4})$

NaOH $F_1(1-w_{w1}) = F_3(1-w_{w3})$

Energy Balance

$F_1 H_1 + F_2 H_2 - \Delta H_r = F_3 H_3 + F_4 H_4$

$$\Delta H_r \sim -2200(w_{w2} - w_{w4}(1 - w_{w2})/(1-w_{w4}))F_2$$

The mass balance equations can be rearranged to yield the required liquid to gas flow rate ratio for any given set of operating conditions:

$$F_1/F_2 = [(1-w_{w2})w_{w4}/(1-w_{w4}) - w_{w2}]/[w_{w1} - w_{w3}(1-w_{w1})/(1-w_{w3})]$$

$$w_{w1} = 0.4 \quad w_{w2} = 0.133 \quad w_{w3} = 0.43 \quad w_{w4} = 0.10$$

$F_1/F_2 = 0.7$ for the dryer example where as a flow ratio of 1 is listed in the report. Substitution of the corrected flow ratio into the energy balance equation yields

$$0.7\ H_1 + H_2 - \Delta H_r = .737\ H_3 + 0.963\ H_4$$

or

$$486\ kJ/kG \approx 476\ kJ/kG$$

where $H_1 = -20.$ $H_2 = 419.$ $H_3 = 65.$ $H_4 = 404.$ $\Delta H_r = -80$ kJ/kG

and the energy balance closes within the error associated with the calculation. Thus, the reported mass and energy balances are approximately correct. Desired operating conditions are achievable.

2.4 Height of a Transfer Unit

The height of a transfer unit is defined as

$$H_{tog} = G/[K_y a\ (1-y)_{*m}]$$

where gas phase resistance dominates and as

$$H_{tol} = L/[K_x a\ (1-x)_{*m}]$$

where liquid phase resistance controls, and can depend on a number of experimental factors including: the gas flux, the specific surface area of the packing, the concentration of the species to be transferred in the gas or liquid phase, temperature, pressure. The importance of the various parameters is determined by the relative magnitude of the resistances encountered in a particular system. The rate of mass transfer through the gas or liquid film may limit the rate of absorption, for example, or the rate of absorption may be controlled kinetically. Heat transfer between the two phases may also prove a limiting factor. See Levenspiel for further details.

Little information is provided for the air-water-NaOH system, and the three possible cases are discussed below in light of an absorber design described in chapter 3.

a) Gas Film Control
For gas film control

$$K_g \approx .1 m/s\ [R\ T]^{-1}$$

and

$$K_y a \approx K_g a P$$

If 0.25 inch Rashig packing is employed, in the dryer example

$$K_y a \approx 220\ moles/(m^3 s)$$

and the height of a transfer unit is ~0.1m.

b) Liquid Film Control
For liquid film control

$$K_l \approx 10^{-5} m\ s^{-1}$$

and

$$K_x a \approx K_l a C_i$$

If 0.25 inch Rashig packing is employed, in the dryer example, and if the enhancement factor is included

$$K_x a \approx 64\ moles/(m^3 s)$$

The height of a transfer unit is ~ 1.0 m.

c) Kinetic Control
Under kinetic control the rates of mass transfer may be substantially lower. This is an unlikely control mechanism.

d) Heat Transfer Control
Heat transfer from the liquid to the gas phase may prove a limiting phenomenon under extreme conditions. Heat transfer coefficients in packed towers are high. For Norton #3 High Pack, for example, the heat transfer coefficient is 2×10^4 J/(m^3 °C s). The heat transfer coefficient for the 0.25 inch Rashig packing is likely to be lower but all heat exchange

requirements will be met with ~ .1 to .2 m of packing.

These calculations are approximate. However, the height of a transfer unit, and therefore the packing depth required, is unlikely to exceed 1.5 m and may be as low as 0.3 m. The required packing depth is substantially lower than the value proposed in the Phase A Study. The required packing depth can be determined experimentally with the proposed apparatus, but it should be noted that the required packing depth varies with packing size, and gas and liquid fluxes. These differences can be predicted with correlations and technical data provided by **Norton, Glitsch**, or other packing suppliers. 1/4 inch Rashig packing may not be employed in an industrial absorber.

2.5 Materials of Construction

Possible materials of construction include: Chlorimet 2 and 3, Durimet 20, furane resins, Monel, and Neoprene. Other materials may also be sufficiently stable. Nickel is subject to stress corrosion cracking above 120 °C in concentrated sodium hydroxide solutions and is not recommended. See the Metals Handbook or other standard references for further details. Monel is recommended for the laboratory apparatus, as valves fittings etc. can be purchased in this material.

2.6 Conclusions

1. Only one transfer unit can be realised in a cocurrent contacting device.
2. Countercurrent operation would be more appropriate in general. However, there is essentially no difference between cocurrent and countercurrent operation if only one transfer unit is required.
3. Contrary to the calculations presented in the study, only one transfer unit is required for the sample paper drying application.
4. If absorption rates are controlled by mass transfer packing depth for the paper drying application is unlikely to exceed 1.5 m, and may be as low as .3 m, at moderate gas fluxes.
5. Enthalpies for sodium hydroxide solutions are presented in an inconsistent manner in the study. Overall mass and energy balances have been verified. Calculated balances are approximately correct.
6. Nickel is a poor choice as a material of construction for this application.
7. The cost of instrumentation is severely underestimated in the Phase A

Study. This matter is discussed in detail in chapter 3.

2.7 Recommendations:

1. A countercurrent contactor/absorber design would be more generally applicable, and is recommended.
2. Corrosion/erosion tests with potentially stable and inexpensive materials should be conducted, so that absorber cost can be minimised.

3. Proposed Laboratory Scale Absorber Apparatus

3.1 Summary

The objective of the laboratory trials is to verify the feasibility of the sodium hydroxide absorber design, while minimising the overall size and complexity of the apparatus. Consequently, only the absorber is modelled with the proposed apparatus. Sodium hydroxide solutions are not regenerated thermally, and air is not recirculated. The absorber is fully instrumented, and can be employed to obtain design and scale-up data for many potential applications of chemical heat pump technology.

The principal constraint imposed on the design of the absorber is the minimum available size of packing material. 0.25 inch Rashig packing is the smallest packing available commercially. This imposes a minimum absorber diameter of approximately 5 cm, and flowrates are scaled accordingly. The apparatus has been designed to operate on a semi-continuous basis, at 4 hour intervals, and will cost in excess of $27 000 to contruct. 50 % of this cost is for instrumentation. Total operating costs, including overhead charges, will depend on the duration of the experimental programme, and are estimated at $5 000 per month.

3.2 Apparatus Design

a) Apparatus Description

The proposed apparatus is a .04% scale partial model of the chemical heat pump and is described with reference to figure 2. Air and steam streams flow through flow controllers and are mixed and heated prior to being fed to the absorber. This moist air stream simulates the effluent air from a drying operation. As steam and compressed air are available on site, no special equipment is required to generate this stream. The moist air stream is dehydrated in the absorber and the effluent is vented. 60 wt% sodium hydroxide solution is pumped from a 60 litre storage vessel through a heater to the absorber. The diluted sodium hydroxide effluent is chilled then mixed with fresh pelletized sodium hydroxide in a 30 litre mixing vessel to raise the concentration to 60 wt %. This solution is then fed to the storage vessel and recycled. At the end of the experimental programme, the sodium hydroxide solution will be recovered for use in undergraduate laboratories. No liquid effluent is produced.

Flow controllers are placed on the air, steam and sodium hydroxide feed

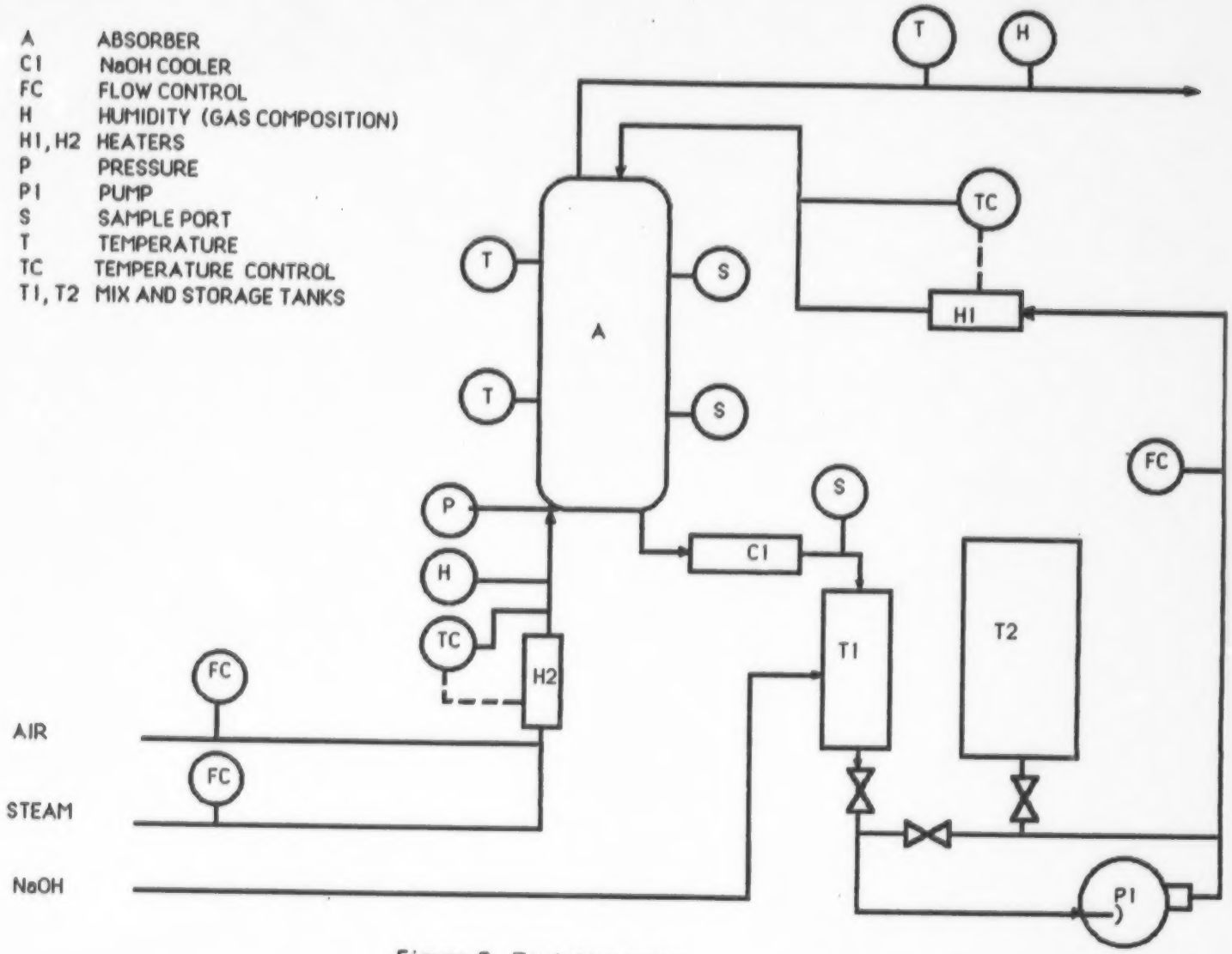

Figure 2: Test Apparatus

lines. These controllers are read and operated manually. The temperature controllers operate automatically. All stream temperatures, the compositions of the two moist air streams, and temperatures at 4 elevations in the absorber are logged on a microcomputer. The gas compositions can be measured directly using hygrometers ($23 000) or determined indirectly using an automatically actuated gas chromatograph with heated sample lines ($10 000).

b) Apparatus Specifications

Principal Components

Absorber - .05 m internal diameter x 1.8 m long Monel tube with removable flanged ends
- 17 1/4 inch drilled sample ports equally spaced along the axis
- packing type: 0.25 inch Monel Rashig rings
- packing depth 1.5 m
- liquid flow rate 6.8 kG/h
- gas flow rate 5.2 kG/h
- demisting mesh 0.1m

Tanks - to be fabricated from 1/16 inch Monel sheet
- the tanks are to be covered and mounted on a stand
- Storage - 60 litres
  - sufficient storage for 100 kG of 60 wt% NaOH solution
- Mix - 30 litres
  - sufficient receiving capacity for a 4h trial

Data Acquisition - PC or XT clone
- Metrabyte analog to digital I/O converter with 16 channels
- Driving software

Hygrometers - two to be supplied by Stephens Equipment Montreal
- high voltage output
- 1 calibrated for 80 °C and 15 wt% moisture
- 1 calibrated for 107 °C and 10 wt% moisture

Gas Chromatograph - TCD detector
- automated sampling with heated sample lines

- heated sample lines are required because the dew point of the feed can exceed 60 °C

c) Equipment Costs

Cost estimates are based on purchase not rental costs. Gas analysis is an expensive element in the experimental programme. Two alternatives are costed in the following table.

Assembly and testing (including overhead costs)			4000.
Temperature controlled line heaters 2x$500			1000.
Pump for NaOH solution			500.
Absorber + Tanks			4000.
Mixer motor			500.
Flow controllers 3x$500			1500.
Data Logging System	Computer	$1500	
	Multiport A/D converter	$2000	
	Software	$ 500	4000.
Thermocouple probes 6x$80			480.
Gas Analysis			
Gas Chromatograph (including heated sample lines)		10000.	
or		or	
Hygrometers 2x$11500		23000.	
Column Packing			500.
Valves 3x$50			150.
NaOH cooler			100.
Insulation			100.
Tubing			400.
Demisting Material			100.
			$27 330.
			or
			$40 330.

d) Operating Costs

The operating costs for a 2 month trial total $10 310. including overhead charges. Overhead charges are determined by the Research Administration at the university and represent a fixed percentage of of direct labour costs.

Labour - Research Engineer	$2500x2x1.65	8910.	
- Supervision	$1000x1.65	1650.	
			9900.
Chemicals			200.
Misc.			200.
			$10 310.

4. Nomenclature

a interfacial area
F_1, F_2, etc. mass flow rates for streams 1 and 2 etc.
G gas flux
H specific enthalpy
H_{tol}, H_{tog} height of a transfer unit
ΔH_r enthalpy of reaction
K_y, K_l, etc. mass transfer coefficients
L liquid flux
N_{tog} number of transfer units
W mass fraction
W_{w1}, etc. mass fraction of water in stream 1, etc.
Y, Y* mole fraction and equilibrium mole fraction in the gas phase

5. References

Glitsch Technical Bulletins
King, C. J.: Separation Processes, 2nd Ed., McGraw Hill, New York, 1980
L venspiel, O.: Chemical Reaction Engineering, 2nd Ed., Wiley, New York, 1972
Metals Handbook, 9th Edition, American Society for Metals, Metals Park, Ohio, 1985
Norton Technical Bulletins
Treybal, R. E.: Mass-Transfer Operations, 3rd Ed., McGraw Hill, New York, 1980